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METAL ION-CONTAINING EPOXIES

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INTRODUCTION

High performance polymers are currently being considered for use as films, coatings, adhesives, and composite matrix resins for future aerospace applications. It is desirable that these materials be able to dissipate lightning charging on aircraft and space charging on spacecraft. Polymers alone have not been able to meet these needs, prompting research efforts to incorporate metal ions into potential aerospace resins.

Palladium ions have been added to polyimides in an effort to increase the electrical conductivity of these polymers for relief of charging effects on space films (1-3). A polyimide containing aluminum ions has also been developed which shows potential as a flexible space film adhesive (4).

Metal ions have been added to epoxies for use as catalytic hardeners (5-6). They have been found to be effective accelerators for anhydride-cured epoxies and for cycloaliphatic epoxies, especially when used in combination with a phenolic accelerator. However, the use of metal ions in epoxies to improve applicability of composite matrix resins for aerospace applications has not been investigated.

The purpose of this research was to incorporate metal ions into an aerospace epoxy composite matrix resin. Metallic and organometallic complexes were added to 5208* epoxy and screened for compatibility, reactivity, thermal stability and mechanical properties.

METAL ION-CONTAINING EPOXIES

OBJECTIVE - INCORPORATION OF METAL IONS INTO AN
EPOXY RESIN FOR AEROSPACE APPLICATIONS

APPROACH - ORGANOMETALLIC COMPLEXES ADDED TO 5208
EPOXY AND SCREENED FOR:

- (1) COMPATIBILITY
- (2) REACTIVITY
- (3) EFFECT ON THERMAL STABILITY
- (4) EFFECT ON MECHANICAL PROPERTIES

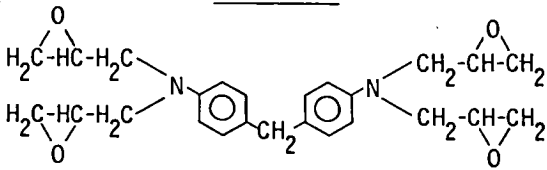
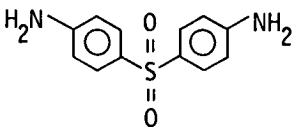
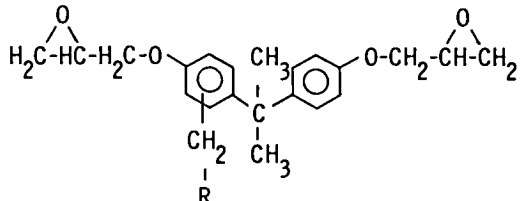
*5208 epoxy resin is a product of Narmco Materials, Inc.

5208 EPOXY RESIN

5208 epoxy resin has been widely used by the aerospace industry as a composite matrix resin. As shown in the figure below, the neat resin has been found to contain tetraglycidyl 4,4'-diaminodiphenylmethane (MY-720) as the major epoxy component, 4,4'-diaminodiphenylsulfone (DDS) curing agent, and a phenolic novolac, SU-8 (7).

This thermosetting resin served as the epoxy control in this investigation. It is a 177°C cure system that yields a very highly crosslinked polymer. Standard solutions were prepared containing 62.5% 5208 solids in methyl ethyl ketone (MEK). This dilution facilitated the addition of metallic complexes to the resin. Neat castings of the control and the metal ion-containing epoxies were obtained by degassing the solutions at 120°C under vacuum and curing to a final cure temperature of 177°C.

COMPOSITION OF 5208 EPOXY RESIN

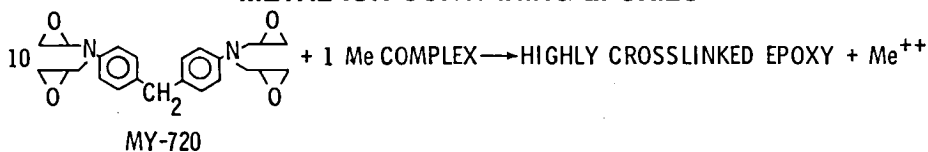
<u>DESIGNATION</u>	<u>COMPONENT</u>	<u>CONCENTRATION (phr)</u>
MY-720		100
DDS		28
SU-8		8.2

METAL ION-CONTAINING EPOXY PREPARATION

A variety of metal and organometallic complexes were investigated as potential additives for 5208 epoxy resin. The nine complexes listed in the table below were added to solutions of 5208 in MEK and stirred at room temperature for two hours. These solutions were poured into aluminum pans and degassed at 120°C under vacuum for 20-35 min. Discs were prepared by gradually heating from 120-150°C over a 2-2½ hour period. The temperature was held at 150°C for approximately 1 hour, then increased to 177°C for a 2 hour final cure. All metal complexes were added at the mole ratio of 1 metal complex for every 10 MY-720 repeat units.

Densities were determined on samples of the cured polymer in a density gradient tube according to ASTM D1505-60T. Those specimens containing the lighter atomic weight metals were less dense than the control, this decrease in density being attributable to the presence of the three bulky acetylacetonate groups. However, with increasing atomic weight of the metal and a larger calculated percent metal content, the epoxy densities increased over that of the control. Because of the pronounced catalytic effect that Li_2PdCl_4 had on the epoxy cure, acceptable specimens could not be obtained with this additive.

METAL ION-CONTAINING EPOXIES



METAL COMPLEX	CALC. % METAL (w/w)	DENSITY (g/cc)	ATOMIC WT. OF METAL
5208 CONTROL	0	1.2717	—
$\text{Al}(\text{acac})_3$	0.42	1.2624	27
$\text{Cr}(\text{acac})_3$	0.81	1.2582	52
$\text{Fe}(\text{acac})_3 \cdot \text{H}_2\text{O}$	0.87	1.2630	56
$\text{Co}(\text{acac})_3$	0.93	1.2605	59
$\text{Ni}(\text{acac})_2 \cdot \text{H}_2\text{O}$	0.94	1.2774	59
$\text{Cu}(\text{acac})_2$	1.02	1.2803	64
Li_2PdCl_4	1.71	—	106
AgNO_3	1.75	1.2880	108
$\text{Th}(\text{acac})_4$	3.50	1.3018	232

GEL TIMES

Gel times were determined at 135°C on a Gel Timer Hot Pot by Shyodu Precision Instrument Co. using 35g of the 1/10 metal complex(Me)/epoxy resins prepared in MEK. Their solution appearance is noted in the table below. Two of the solutions, those containing Co and Cr ions, became opalescent after 1-2 hours of stirring. Before determination of gel times, the solutions were degassed under vacuum at 120°C to remove the MEK.

The 5208 control gelled in 152 min. at 135°C. The addition of Ni and Al ions inhibited the epoxy cure at this temperature. Insolubility of the Ni and Al complexes in the 5208 at 135°C seemed to be a contributing factor to the cure inhibition of these formulations. All other metal ions were more soluble at this temperature and accelerated the cure. Acceleration was so dramatic with Pd/5208 that the solution auto-ignited after 7 minutes.

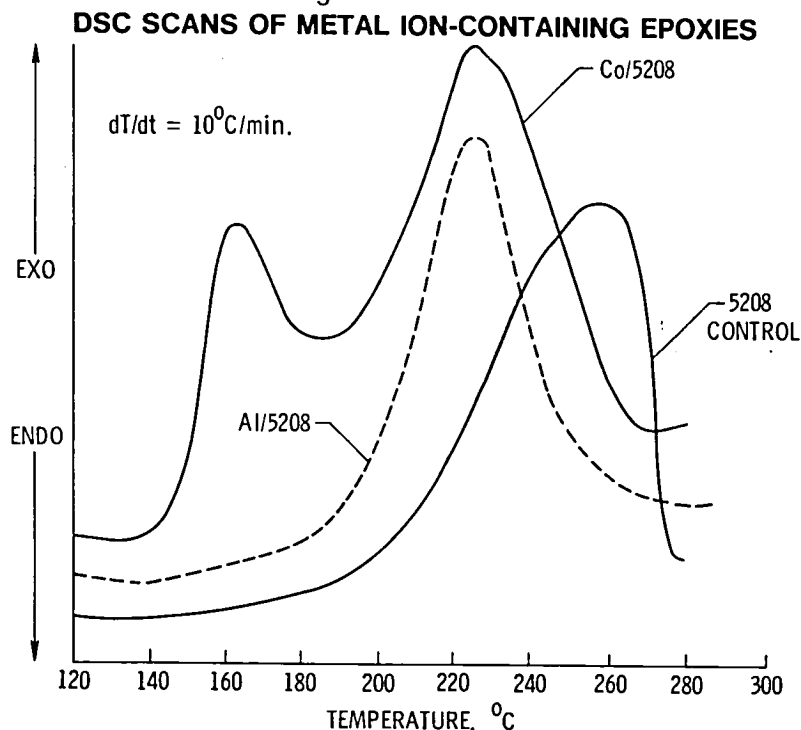
GEL TIMES OF METAL ION-CONTAINING EPOXIES

METAL COMPLEX/5208	GEL TIME AT 135°C, min.	EPOXY SOLUTION APPEARANCE
Ni	220	MILKY BLUE/GREEN
Al	172	MILKY GRAY/BROWN
5208	152	TRANSPARENT GOLD
Cr	114	OPALESCENT PURPLE
Ag	107	OPAQUE OLIVE GREEN
Cu	102	OPAQUE GRAY/BLUE
Fe	40	MILKY RUST
Co	17	OPALESCENT GREEN
Th	14	MILKY HONEY
Pd	7	OPAQUE DK. BROWN/ORANGE

CURE EXOTHERMS

Differential scanning calorimetry (DSC) was used to obtain the cure exotherms of the metal ion-containing epoxies. The scans were obtained on a DuPont 990 Thermal Analyzer/Differential Scanning Calorimeter using a programmed heating rate of $10^{\circ}\text{C}/\text{min}$. Prior to the DSC runs, each epoxy solution was degassed under vacuum for 35 min. at 120°C to remove the methyl ethyl ketone solvent. As shown below, the 5208 control showed a single exotherm at 264°C . All cure exotherms of the metal ion-containing epoxies occurred at lower temperatures than that of the control, even those that were found to inhibit the epoxy cure by gel time determinations at 135°C . The insolubility of the Ni and Al complexes and the resulting inhibition of the epoxy cure was eliminated as the DSC temperature was increased above the 177°C final cure temperature of the epoxy. Me/epoxy resins containing Fe, Al, Cr, and Ag ions showed single peak behavior with exotherms occurring at 216, 226, 255 and 268°C , respectively. However, two exotherm peaks were observed for 5208 containing Ni, Th, Cu, Pd and Co ions. In each case one of the peaks appeared as a shoulder of the other, with the exception of Co/5208. The two peaks in the cobalt-containing epoxy were more distinctly resolved with a wider separation between peaks. The initial exotherm for this polymer occurred at 158°C which was at least 20°C earlier than for all other Me/epoxy systems studied.

The second peak or shoulder in these Me/epoxy DSC spectra is attributed to the presence of the metal complex. Similar behavior has been reported for an MY-720 based epoxy containing BF_3 (8).



GLASS TRANSITION TEMPERATURES

Apparent glass transition temperatures (T_g 's) of the cured epoxies were determined both on a DuPont Model 943 Thermomechanical Analyzer (TMA) at a heating rate of 10°C/min using a penetration probe and on a DuPont 1090 Thermal Analyzer/981 Dynamic Mechanical Analyzer at a heating rate of 5°C/min. Regardless of the method used, the addition of a metal complex to the 5208 resin consistently lowered the apparent T_g as shown in the table below. The Al/5208, Ni/5208 and control showed evidence of further cure by DMA as indicated by a second T_g peak at elevated temperature. Both the Al and Ni complex were previously shown to be inhibitors by gel time determinations.

Those epoxies containing metal ions that accelerated the cure showed only one high temperature transition. However, this transition occurred at a lower temperature than that of the control.

GLASS TRANSITION TEMPERATURES OF Me/EPOXIES

Me COMPLEX/5208	T_g BY TMA ^(a) (°C)	T_g BY DMA ^(b) (°C)
5208	221	247 (284)
Ag	205	242
Cr	198	224
Ni	187	209 (264)
Cu	185	204
Co	177	195
Al	175	178 (254)
Fe	172	198
Th	155	173

(a) $dT/dt = 10^\circ\text{C}/\text{min}$

(b) $dT/dt = 5^\circ\text{C}/\text{min}$

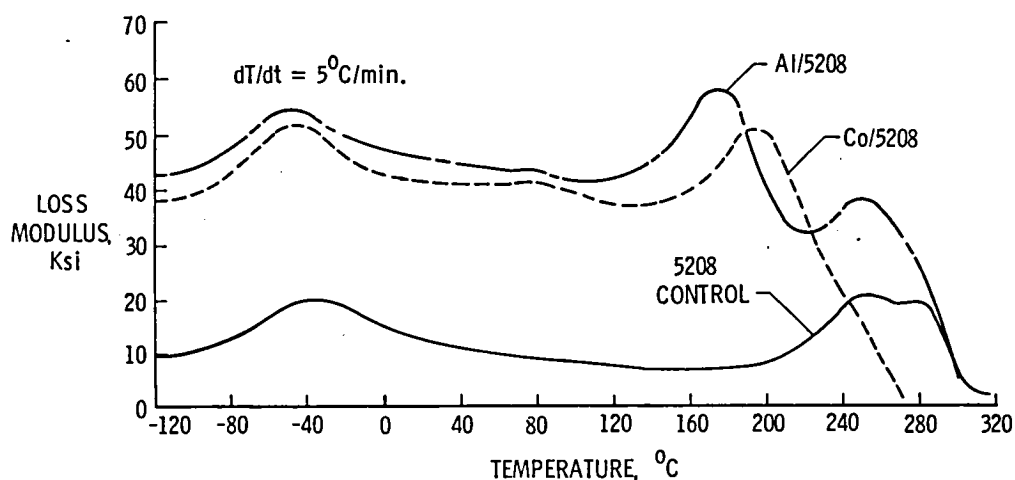
DYNAMIC MECHANICAL ANALYSIS SPECTRA

DMA curves of the 5208 epoxy containing a metal ion inhibitor and accelerator are compared with that of the control in the figure below. These spectra are representative of all the metal ion-filled epoxies studied. All three materials showed a low temperature β -transition characteristic of segmental motion in the polymer chain. The 5208 control exhibited a peak at 247°C indicative of its T_g , followed closely by a shoulder which is attributed to some additional crosslinking.

The DMA curve of the epoxy containing the Al ion inhibitor showed two widely separated transitions at elevated temperature, a T_g peak at 178°C followed by a second peak at 254°C. It is understandable that an epoxy containing an additive which inhibits the cure should undergo additional crosslinking after exposure to higher temperatures.

The DMA curve of an epoxy containing Co ions, previously found to accelerate the cure, is also shown below. This fully-cured polymer shows no evidence of additional crosslinking, exhibiting only a single T_g peak at 195°C.

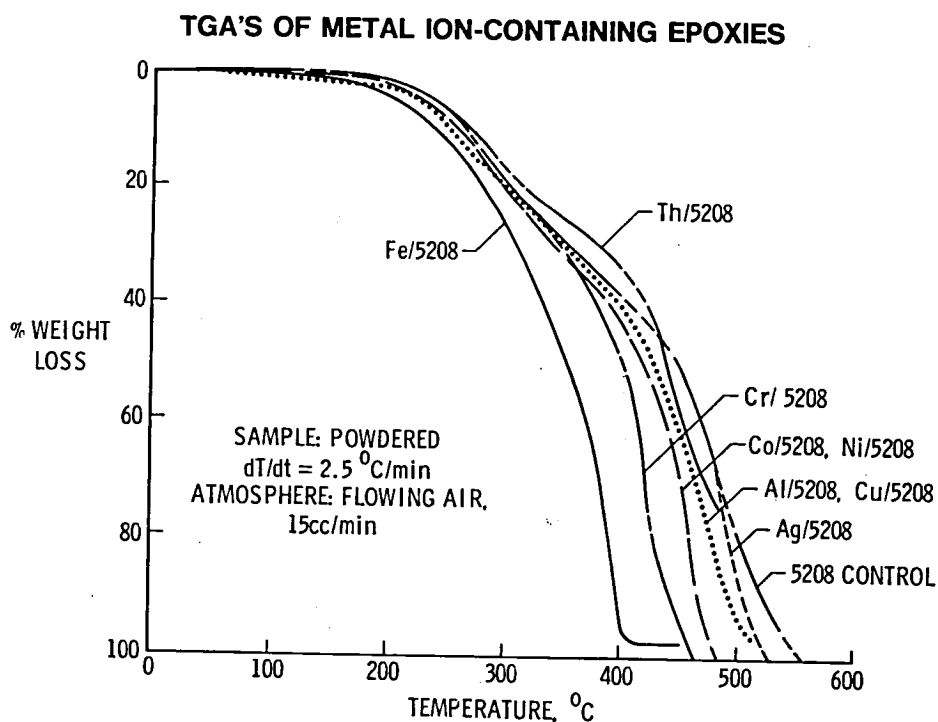
DMA'S OF METAL ION-CONTAINING EPOXIES



THERMOGRAVIMETRIC ANALYSIS (TGA)

The thermooxidative stability of powdered epoxy samples was measured in flowing air (15 cc/min) on a Perkin Elmer Model TGS-2 Thermogravimetric System using an AR-2 Autobalance and a UU-1 Temperature Program Control at a heating rate of 2.5°C/min.

As shown in the curves below, the percent weight loss for the control and for the majority of the metal ion-containing epoxies was quite similar at temperatures below 350°C. Exceptions included the iron-containing epoxy, which exhibited poorer thermal stability, and Th/5208, which was more stable than the control below 450°C.



MECHANICAL STRENGTH AND STIFFNESS

Flexural properties were determined at room temperature on neat resin castings of the metal-ion containing epoxies. Tests were run using an Instron Testing Machine Model TT-C in a three-point bending mode. Initial screening tests were performed using one or two specimens whose dimensions averaged $6.35 \text{ mm} \times 1.27 \text{ mm} \times 25.4 \text{ mm}$ at an average span/thickness of 16/1 as specified by ASTM Standard D790-71. These preliminary results are listed below. Most systems showed a decrease in flexural strength and a modest increase in modulus. Co/5208 was the exception. Because of the dramatic increase in flexural strength achieved with the cobalt-containing epoxy, the control and the Co/5208 materials were retested using five samples each. The addition of $\text{Co}(\text{acac})_3$ to 5208 epoxy resulted in an impressive 95% increase in flexural strength and 35% increase in modulus, accompanied by a 41% decrease in percent elongation.

Such pronounced improvements in mechanical properties of Co/5208 may be linked to the mechanism of cure and resulting network structure. As previously discussed, only the Co/5208 system showed two distinct and widely separated cure exotherms by DSC, the first occurring 106°C earlier than the exotherm for the control. It is possible that the cobalt-accelerated cure of this epoxy may lead to the formation of a stronger, more continuous secondary microgel network. Such behavior, as suggested by Misra et al. (9), would improve the mechanical strength of the cured epoxy resin.

PRELIMINARY FLEXURAL PROPERTIES OF Me/EPOXIES

Me COMPLEX/5208	FLEX STR, ksi	FLEX MOD, ksi	PERCENT ELONGATION
5208	18.2*	460	4.1
Cu	10.8	600	1.9
Th	12.6	490	0.2
Fe	13.3	460	1.7
Ni	15.8	500	3.2
Ag	16.0	560	2.9
Cr	16.3	480	3.7
Al	20.6	570	4.5
Co	35.4*	620	2.4

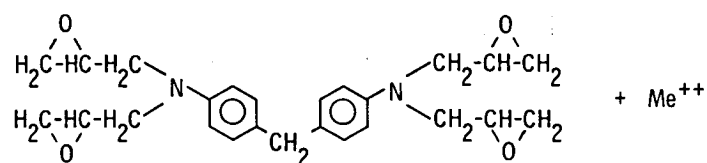
*THESE DATA POINTS REPRESENT THE AVERAGE OF FIVE SAMPLES, WITH A VARIABILITY OF $\pm 18\%$ FOR 5208 AND $\pm 10\%$ FOR Co.

CONCLUSIONS

Metal ion-containing epoxies were prepared using a variety of metal and organometallic complexes incorporated into 5208, an aerospace epoxy matrix resin. The addition of Cr, Co, Ag, Fe, Cu, Th and Pd were found to accelerate the epoxy cure, while Ni and Al inhibited it. Significant differences in the cure exotherms of these epoxies were noted by differential scanning calorimetry. The addition of metal complexes to 5208 lowered the glass transition temperature of cured castings as measured by thermomechanical analysis and dynamic mechanical analysis. Mechanical properties were determined at room temperature for the doped systems. The cobalt-containing epoxy exhibited a 95% increase in flexural strength and a 35% increase in flexural modulus compared to that of the control.

The use of the Ni and Al ion inhibitors in combination with metal ion accelerators in the 5208 epoxy will be further investigated. It is hoped that the presence of an inhibiting ion will slow the epoxy cure enough to allow for higher level loadings of advantageous metal complexes. The high strength cobalt-doped epoxy will be further evaluated for its potential as an aerospace composite matrix resin.

EPOXIES CONTAINING METAL IONS



- METAL IONS HAVE BEEN SUCCESSFULLY INCORPORATED INTO A HIGHLY CROSSLINKED AIRCRAFT EPOXY
- Cr, Co, Ag, Fe, Cu, Th AND Pd ACCELERATE EPOXY CURE
- Al, Ni INHIBIT EPOXY CURE
- INITIAL RESULTS SHOW Co IMPROVES STRENGTH AND STIFFNESS

POTENTIAL APPLICATIONS

MATRIX RESINS FOR ADV. AIRCRAFT AND SPACECRAFT

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16. Abstract A variety of metallic and organometallic complexes have been investigated as potential additives for an epoxy currently used by the aerospace industry as a composite matrix resin. A total of 9 complexes have been screened for compatability and for their ability to accelerate or inhibit the cure of a highly crosslinkable epoxy resin. Methods for combining the metallic complexes with the resin have been investigated, gel times recorded, and cure exotherms studied by differential scanning calorimetry. Glass transition temperatures of cured metal ion-containing epoxy castings were determined by thermomechanical analysis. Thermal stabilities of the castings were determined by thermogravimetric analysis. Mechanical strength and stiffness of these doped epoxies have also been measured.					
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